Zincian carbonates from the oxidized zone of the Waryński mine, Upper Silesia, Poland, were analyzed by AEM techniques. Compositions lie in the system CaCO₃-MgCO₃-(Fe,Mn)CO₃-ZnCO₃, within three one-phase areas of CaCO₃-rich, dolomite, and CaCO₃-poor solid solutions similar to those in the system CaCO₃-MgCO₃-FeCO₃ (Rosenberg, 1967). Dolomite solid solutions extend from CaMg(CO₃)₂ to at least 72 mol% CaZn(CO₃)₂ and have electron-diffraction patterns consistent with the R3 dolomite structure. The extent of solid solution is greater toward CaZn(CO₃)₂ than toward CaFe(CO₃)₂ in the system CaCO₃-MgCO₃-FeCO₃ at higher temperatures. However, neither of these end-members has been observed in nature or synthesized. CaCO₃-poor solid solutions approach the system FeCO₃-ZnCO₃ whereas CaCO₃-rich solid solutions are close in composition to the CaCO₃ end-member.

Analyses of carbonates from the Waryński mine and from Tsumeb, Namibia (Garavelli et al., 1982), as well as inferences from experimental studies (Goldsmith, 1983) suggest that the dolomite end-member CaZn(CO₃)₂ may be stable at low temperatures.

**INTRODUCTION**

Phase relationships in the system CaCO₃-MgCO₃-ZnCO₃ and the extent of Zn substitution for Mg in the dolomite structure are long-standing problems in the geochemistry of the carbonates. Advances in our knowledge of this system have come slowly because of the rarity of these carbonates in nature and because of the almost complete lack of experimental data.

Dolomites containing significant amounts of Zn were first described from Tsumeb, Namibia, by Hurlbut (1957), but Ca in these dolomites was partially replaced by Pb. More recently, several Zn-rich, Pb-free dolomites have been described from the same locality (Garavelli et al., 1982). A carbonate approaching CaZn(CO₃)₂ in composition and showing evidence of cation ordering consistent with the dolomite space group, R3, was identified, characterized, and named minrecordite. It occurs within a zone of oxidation with dioptase, CuSiO₃(OH)₂, and, therefore, is thought to have crystallized at low temperature.

Although a thorough study of the system CaCO₃-ZnCO₃ has never been attempted, some data at 600 and 750 °C have been published (Goldsmith and Northrup, 1965). Subsolidus relations are similar to those in the system CaCO₃-FeCO₃, in that extensive immiscibility exists and an ordered compound was not observed. However, the maximum thermal stability of CaZn(CO₃)₂ may lie below 600 °C (Goldsmith, 1983).

Experimental data are not available for the system CaCO₃-MgCO₃-ZnCO₃, but on the basis of octahedral distortion, Rosenberg and Foit (1979) predicted that the extent of substitution of Zn for Mg in the dolomite structure is greater than that for Fe²⁺. Thus, considering all lines of evidence, a dolomite composition approaching end-member CaZn(CO₃)₂ is probably stable at a maximum temperature that lies below 600 °C. However, much more data are required to define phase relations in the ternary system.

In 1959, Zabiński described a zincian dolomite with a Zn/Mg ratio close to unity from the Waryński mine, near Bytom, Upper Silesia, Poland; the zincian dolomite occurred in an assemblage with calcite, smithsonite, goethite, and gypsum. The fine grain-size of the minerals in this assemblage precluded separation of zincian dolomite for purposes of characterization. Identification was based on X-ray powder diffraction and chemical analyses of bulk samples after leaching to remove smithsonite and gypsum. In a later study (Jasińska and Zabiński, 1972), electron-microprobe analyses confirmed the chemical composition of zincian dolomite inferred earlier and revealed that Zn is unevenly distributed in dolomite grains. Zincian dolomite occurs on grain rims and in the cement between grains, suggesting that it formed during the final stages of dolomitization. Electron-microprobe analyses of discrete dolomite grains were obtained, but the resolution was not adequate to provide analyses of zones within grains.

A sample of the zincian dolomite-bearing assemblage
was obtained for analysis by means of analytical electron microscopy (AEM) through the kindness of Dr. W. Zabiński, Institute of Geology and Mineral Deposits, Academy of Mining and Metallurgy, Krakow, Poland. It was anticipated that this investigation would test predictions of the extent of Zn substitution for Mg in the dolomite structure and provide a further insight into phase relations in the system CaCO₃-MgCO₃-ZnCO₃.

**Procedures**

Although the sample was received as a fine powder, the crystals were too thick for “thin specimen” analysis (Lorimer, 1987). Therefore, the sample was ground lightly under ethanol and air-dried before it was deposited from a distilled water suspension onto C-covered grids. Inasmuch as textural relationships were destroyed by grind-
ing, the coexistence of phases and their compositions in successive zones could not be determined. Further studies in which grains are mounted in an epoxy resin and thinned by ion milling would be of interest and may be possible if suitable samples can be obtained.

Isolated crystals transparent to the electron beam (100 kV) in the TEM mode were selected for AEM analyses. Elemental ratios were determined using a Philips EM400T electron microscope equipped with an EDAX energy-dispersive X-ray detector, following procedures reviewed by Lorimer (1987). The analyses (60-s live time) were quantified using proportionality constants that had previously been obtained for Mg, Ca, Fe, and Mn from well-characterized silicate standards (Cliff and Lorimer, 1975) and for Zn from a homogenized Al-Zn-Mg alloy. The total relative errors in elemental analyses have been calculated at the 2σ confidence level based on X-ray (Gaussian) counting statistics and assuming an error of ±2% in the proportionality constant (Lorimer, 1987). For typical Ca- and Zn-rich analyses, the relative error is approximately ±3.0% for Ca, ±4.7% for Mg, ±11.1% for Mn, ±6.1% for Fe, and ±3.2% for Zn.

Electron diffraction was used to determine whether the zincian carbonates with Ca/(Zn + Mg + Fe + Mn) ratios approximating unity have the ordered dolomite structure, space group R3 or the calcite structure, space group R3c. The c glide in the calcite space group leads to systematic absences for reflections of the type hh0l when l is odd. However, because of the double diffraction that occurs with electrons in samples of any significant thickness, the only zone axis that will show the absence or presence of the relevant reflections, and thus of the c-glide plane, is (100) (Figs. 1a, 1b).

Because only a small amount of sample was available, X-ray diffractometry was not attempted in this study. X-ray powder-diffraction data for this material was published in an earlier study (Zabinski, 1959).

RESULTS AND IMPLICATIONS

Semi-quantitative, preliminary AEM analyses were carried out in order to identify the minerals present in the sample. A great many of the grains were found to be rhombohedral cleavage fragments, presumably carbonates. Most of these crystals have compositions lying in the system CaCO₃-MgCO₃-MnCO₃-FeCO₃-ZnCO₃, although end-member CaCO₃ and ZnCO₃ were also observed. Gypsum, an unidentified calcium silicate, and Fe-rich, formless masses, thought to be goethite, are present in small proportions.

One hundred crystalline grains with compositions in the system CaCO₃-MgCO₃-MnCO₃-FeCO₃-ZnCO₃ were analyzed quantitatively using AEM techniques. Based on their chemical compositions, 65 of these analyses are thought to represent dolomites, 21 calcites, 8 siderites, and 6 smithsonites.

Electron-diffraction patterns of typical compositional analogues of dolomite were found to be consistent with the dolomite structure. Three grains containing more than 20 mol% ZnCO₃ were tilted in reciprocal space until the (100) zone axis was parallel to the electron beam. All three showed the same pattern. The diffraction pattern in Figure 1c was obtained from a grain with a composition of 49 mol% CaCO₃, 20 mol% MgCO₃, 0 mol% MnCO₃, 2 mol% FeCO₃, and 29 mol% ZnCO₃. It is identical to the pattern in Figure 1a and can, therefore, be indexed as belonging to the R3 (dolomite) rather than the R3c (calcite) space group.

Carbonate compositions in the five-component system expressed in terms of the end-members CaCO₃, (Mg,Fe,Mn)CO₃, and ZnCO₃ are shown in Figure 2 along with the boundaries of the one-phase areas in the system CaCO₃-MgCO₃-FeCO₃ at 450 °C (dashed lines; Rosenberg, 1967). Most of the analyses lie within or close to these one-phase areas, suggesting that subsolidus relations in the system CaCO₃-(Mg,Fe,Mn)CO₃-ZnCO₃ are similar to those in the system CaCO₃-MgCO₃-FeCO₃. Both systems are dominated by three one-phase areas of CaCO₃-rich, dolomite, and CaCO₃-poor solid solutions, separated by extensive two-phase areas. The Fe and Zn analogues of dolomite, CaFe(CO₃)₂ and CaZn(CO₃)₂, have not been observed. The few analyses that lie between one-phase areas are thought to represent mixtures of two phases.

The compositional analogues of dolomite are also
The zincian dolomites from the Waryński mine occur in the zone of oxidation of a Pb-Zn ore deposit where they formed as a result of metasomatic alteration of pre-existing dolomites under supergene conditions (Zabiński, 1980). Minrecordite and associated zincian dolomites from Tsumeb, Namibia, formed under similar conditions (Garavelli et al., 1982), although apparently not from pre-existing dolomites by replacement of Mg by Zn. Crystallization temperatures of the zincian dolomites and the siderite-smithsonite solid solutions reported by Bak and Zabiński (1981) must have been low.

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tures, but more evidence is required to confirm this inference. If minrecordite (92 mol% CaZn(CO₃)_2) is a single-phase member of a continuous dolomite solid-solution series, then the stability of the end-member CaZn(CO₃)_2 would be highly likely, but its stability limits and phase relations would still require investigation. Because Zn-rich dolomites are rare in nature, an experimental investigation of stability relationships in the system CaCO₃-MgCO₃-ZnCO₃ would be desirable.

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